



Draft EPA Region 4 Suggested Practices for Evaluation of a Site For Natural Attenuation (Biological Degradation) of Chlorinated Solvents¹

November, 1999

<http://www.epa.gov/region4/>

Version 3.1

¹This document was formerly titled **Draft Region 4 Approach to Natural Attenuation of Chlorinated Solvents**

Table of Contents

Overview of the Technical Protocol	Page 5
Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation	Page 7
Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation	Page 8
Behavior of Chlorinated Solvent Plumes	Page 9
Protocol for Quantifying Biological Degradation During the Remedial Investigation Process	Page 10
Determining Whether Biodegradation is Occurring	Page 13
Groundwater Characterization	Page 18
Refine the Conceptual Model, Complete Premodeling Calculations, and Document Indicators of Biological Degradation	Page 21
References	Page 23
Appendix	Page 27



Draft EPA Region 4 Suggested Practices for Evaluation of a Site For Natural Attenuation (Biological Degradation) of Chlorinated Solvents²

This document is an amalgamation of technical information obtained from the Draft AFCEE³ *Protocol for Evaluation of Natural Attenuation of Chlorinated Solvents in Ground Water*, articles in professional journals, and meeting presentations by experts in the field (see references).

Preface

The intent of this document is to provide a resource for the characterization of sites where natural attenuation (biological degradation) is being proposed or considered. Region 4 wishes to specify that the Draft Interim Final OSWER Directive on Monitored Natural Attenuation (OSWER Directive 9200.4-17 available on the web at <http://www.epa.gov/swerust1/directiv/d9200417.htm>). The Directive is a complement to this document. The hope within EPA nationwide is that a guidance document will be put forth from EPA's Office of Research and Development that will also compliment or supersede this document. This document is now available at <ftp://ftp.epa.gov/pub/ada/reports/protocol.pdf>

The **Draft EPA Region 4 Suggested Practices for Evaluation of a Site for Natural Attenuation (Biological Degradation) of Chlorinated Solvents** is being provided by U.S. EPA Region 4 in DRAFT form due to the evolving nature of the research being performed in labs and on sites on the biological degradation of chlorinated solvents in ground water. In addition, on sites where natural attenuation is being implemented and/or considered, site characterization methods, analytical methods and sampling techniques are changing rapidly. The site characterization for karst and fractured rock would be subject to additional requirements.

At a minimum U.S. EPA Region 4 expects the following in a natural attenuation demonstration report: 1) a site characterization presented and supported, 2) remedial action for the 'source' to be provided 3) a long term monitoring (including O&M) plan provided, 4) a comparison of the natural attenuation remedy (if this is an appropriate determination for the site) to an engineered remedy, 5) the enumeration of institutional controls that are currently operational and enforceable for the site and 6) determination of the carbon source and it's sustainability for chlorinated solvent degradation.

If you have comments or questions concerning this document contact Kay Wischkaemper at 404-562-8641 or wischkaemper.kay@epamail.epa.gov. The web page location is <http://www.epa.gov/region4/wastepgs/oftecser/protoexp.pdf>.

Introduction

Region 4 acknowledges that natural attenuation due to advection, adsorption, biological degradation, dispersion, and volatilization can effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the ecosystem. Natural attenuation in conjunction with source treatment can be the sole remedial alternative for many sites in Region 4. The framework behind the evaluation requirements in this document are The National Contingency Plan (NCP) citations which are the basis for Natural Attenuation remedy selections made in EPA Region 4.

'...Natural attenuation is generally recommended only when active restoration is not

²This document was formerly titled **Draft Region 4 Approach to Natural Attenuation of Chlorinated Solvents**

³Air Force Center for Environmental Excellence

practicable, cost effective or warranted because of site-specific conditions (e.g., Class III ground water or ground water which is unlikely to be used in the foreseeable future and there fore can be remediated over an extended period of time) or where natural attenuation is expected to reduce the concentration of contaminants in the ground water to the remediation goals-levels determined to be protective of human health and sensitive ecological environments--in a reasonable time-frame. Further, in situations where there would be little likelihood of exposure due to the remoteness of the site, alternate points of compliance may be considered, **provided contamination in the aquifer is controlled from further migrations**. The selection of natural attenuation by EPA does not mean that the ground water has been written off and not cleaned up but rather that biodegradation, dispersion, dilution, and adsorption will effectively reduce contaminants in the ground water to concentrations protective of human health in a time frame comparable to that which could be achieved through active restoration (p.8734).

Another NCP citation stating EPA's position on ground water that is not a current source of drinking water but has the ability to be used for drinking water purposes is:

...It is EPA policy to consider the beneficial use of the water and to protect against current and future exposures. Ground water is a **valuable resource** and should be protected and restored if necessary and practicable...(p. 8733)

The expectation of EPA in the above citations is that ground water will be restored and when natural attenuation and source treatment are determined to be the appropriate remedial alternative, or part of a remedial alternative for site ground water, the following provisions are understood.

- Measures are taken to "cut off" continued addition of contaminants to ground water and control migration of contaminants in ground water. This embodies removing, remediating, and/or containing the source (see NCP and OSWER Directive No. 9283.1-2).
- All portions of the plume within the area of attainment shall be remediated to the ground water protection standard's which are MCL's, non-zero MCLG's and health-based standards for current and potential sources of drinking water. An onsite (within the site property boundary) downgradient compliance boundary will be established beyond which accepted limits cannot be exceeded so that further degradation of large expanses of uncontaminated ground water will be prevented. In other words, the condition in which the property boundary is at a significant distance from the plume the compliance boundary must be located near the existing terminus of the plume. Additionally the area of contamination that exceeds the standards may not be allowed to increase prior to attenuation or discharge into surface water (see NCP and OSWER Directive No. 9283.1-2).

Institutional controls are required to ensure that such ground waters are not used before levels protective of human health are reached. On DOE and some DoD sites the enforceable institutional control issue is more easily provided for; whereas on RCRA and CERCLA sites this poses a considerable problem.

Another issue that is of concern regulatorily is the condition where plume 'starvation' occurs. In short, this is where the carbon source necessary for biological degradation of chlorinated solvents runs out and the plume is back to the concentrations that could exceed the ground water protection standards. This 'starvation' issue forces the need for identifying what that carbon source is and making a prediction about the ability of the carbon source to sustain biological degradation of the solvent plume. When identifying the carbon source is not possible, then long term monitoring will be the sole method of ensuring that biological degradation will continue until the contaminant concentrations are below the ground water protection standard. This poses a problem with predicting the length of time for biological degradation to occur and the ultimate cost of using intrinsic degradation as part of the final remedial alternative.

The U.S. Environmental Protection Agency's (EPA) Office of Research and Development and Office of Solid Waste and Emergency Response define natural attenuation as:

The biodegradation, dispersion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to

levels that are protective of human health and the ecosystem.

Natural attenuation processes, such as biodegradation, can often be dominant factors in the fate and transport of contaminants. Thus, consideration and quantification of biodegradation processes is essential to more thoroughly understand contaminant fate and transport.

This paper presents suggested practices for data collection and analysis for the evaluation of a remedial option of natural attenuation (through biological degradation processes). In some cases, the information collected using this protocol will show that natural attenuation processes, with or without source removal, will reduce the concentrations of these contaminants to below risk-based corrective action criteria or will attain regulatory standards within an acceptable, site-specific time period.

Overview of the Technical Protocol

Natural attenuation in ground-water systems results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Biodegradation is the most important destructive attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization.

Biodegradation of fuel hydrocarbons, especially benzene, toluene, ethyl benzene, and xylenes (BTEX), is mainly limited by electron acceptor availability, and biodegradation of these compounds generally will proceed until all of the contaminants are destroyed. In the experience of many researchers, there appears to be an inexhaustible supply of electron acceptors in most, if not all, hydrogeologic environments. On the other hand, the more highly chlorinated solvents (e.g., perchloroethene and trichloroethene) typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the chlorinated aliphatic hydrocarbons) and an adequate supply of electron donors. Electron donors include fuel hydrocarbons or other types of anthropogenic carbon (e.g., landfill leachate, BTEX, or natural organic carbon). If the subsurface environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are removed, reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. The need for adequate electron donors is the most significant difference between the processes of fuel hydrocarbon and chlorinated aliphatic hydrocarbon biodegradation. For this reason, it is more difficult to predict the long-term behavior of chlorinated aliphatic hydrocarbon plumes than fuel hydrocarbon plumes. Thus, it is important to have a thorough understanding of the operant natural attenuation mechanisms.

In addition to having a better understanding of the processes of advection, dispersion, dilution from recharge, and sorption, it is necessary to better quantify biodegradation. Quantification of biodegradation requires a thorough understanding of the interactions between chlorinated aliphatic hydrocarbons, anthropogenic/natural carbon, and inorganic electron acceptors at the site. Detailed site characterization is required to adequately understand these processes.

The proponent must scientifically demonstrate that biodegradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment in order to support remediation by natural attenuation. Three lines of evidence can be used to support biological degradation of chlorinated solvents:

1. Observed reduction in contaminant concentrations along the flow path downgradient from the source of contamination;
2. Documented loss of contaminant mass at the field scale:
 - Using chemical and geochemical analytical data (e.g., decreasing parent compound concentrations, increasing daughter compound concentrations, depletion of electron acceptors and donors, and increasing metabolic byproduct concentrations);
 - A conservative tracer and a rigorous estimate of residence time along the flow path to document contaminant mass reduction and to calculate biological decay rates at the field scale.

3. Microbiological laboratory⁴ or field data that support the occurrence of biodegradation and give rates of biodegradation.

In an evaluation for the demonstration of biological contaminant degradation, the investigator must obtain either the first two lines of evidence.

The second and third lines of evidence are crucial to the natural attenuation demonstration of biodegradation because they provide biodegradation rate constants. The biodegradation rate constants are used in conjunction with the other fate-and-transport parameters to predict contaminant concentrations and to assess risk at downgradient points of compliance.

The first line of evidence is simply an observed reduction in the concentration of released contaminants down-gradient from the NAPL source area along the groundwater flow path. The observed reduction does not prove that contaminants are being destroyed because the reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization with no loss of contaminant mass. Conversely, an increase in the concentrations of some contaminants, most notably degradation products such as vinyl chloride, could be indicative of natural attenuation.

The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed via biodegradation, not just diluted. The second line of evidence is divided into two components. The first component is the use of chemical analytical data in mass balance calculations to show that decreases in contaminant and electron acceptor and donor concentrations can be directly correlated to increases in metabolic end products and daughter compounds. The mass balance calculation can be used to show that electron acceptor and donor concentrations in ground water are sufficient to facilitate degradation of dissolved contaminants. Solute fate-and-transport models can be used to aid mass balance calculations and to collate information on degradation. The second component is the use of measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters, such as seepage velocity and dilution, to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The third line of evidence, microbiological laboratory data, can be used to provide additional evidence that indigenous biota are capable of degrading site contaminants at a particular rate. The most useful type of microbiological laboratory data is the microcosm study, because it is necessary to show that biodegradation is occurring and to obtain biodegradation rate constants.

This paper presents a technical course of data gathering that allows converging lines of evidence to be used to scientifically document the occurrence and quantify the rates of natural attenuation. Ideally, the first two lines of evidence should be used in the natural attenuation demonstration. To further document natural attenuation, or at sites with complex hydrogeology, obtaining a field-scale biodegradation rate may not be possible; in this case, microbiological laboratory data can be used. Such a "weight-of-evidence" approach will greatly increase the likelihood of successfully verifying natural attenuation at sites where natural processes are restoring the environmental quality of ground water.

Collection of an adequate database during the iterative site characterization process is an important step in the documentation of natural attenuation. Site characterization should provide data on the location, nature, and extent of contaminant sources. Site characterization also should provide information on the location, extent,

⁴Microcosm studies are strongly influenced by the nature of the geologic material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Noted here is that some researchers feel that microcosm studies for low levels of contamination are difficult to perform. In some cases the microcosm is 'killed' prior to any data being obtained to evaluate rate constants. Some researchers feel that rate constants obtained from microcosm studies are significant underestimates of actual conditions and therefore in some cases are not useful. In other cases microcosm studies are a productive tool with the following stipulation: if additional evidence (beyond contaminant and geochemical data and supporting calculations) supporting biological degradation is required, a microcosm study using site-specific aquifer materials and contaminants can be undertaken. An overall suggestion is that because microcosm studies are time-consuming and expensive, they should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of contaminants.

and concentrations of dissolved contamination; ground-water geochemical data; geologic information on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential contaminant migration pathways to human or ecological receptor exposure points. The data collected during site characterization can be used to simulate the fate and transport of contaminants in the subsurface. Such simulation allows prediction of the future extent and concentrations of the dissolved contaminant plume. Several models⁵ can be used to simulate dissolved contaminant transport and attenuation. The natural attenuation modeling effort has three primary objectives: 1) to predict the future extent and concentration of a dissolved contaminant plume by simulating the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the potential for downgradient receptors to be exposed to contaminant concentrations that exceed regulatory or risk-based levels intended to be protective of human health and the environment; and 3) to provide technical support for the natural attenuation remedial option at postmodeling regulatory negotiations to help design a more accurate verification and monitoring strategy and to help identify early source removal strategies.

Upon completion of the fate-and-transport modeling effort, model predictions can be used in an exposure pathways analysis. If natural attenuation is sufficient to mitigate risks to potential receptors, the proponent of natural attenuation has a reasonable basis for negotiating this option with regulators. The exposure pathways analysis allows the proponent to show that potential exposure pathways to receptors will not be completed.

Overview of Chlorinated Aliphatic Hydrocarbon Biodegradation

An accurate estimate of the potential for natural biodegradation is important to obtain when determining whether ground-water contamination presents a substantial threat to human health and the environment, because biodegradation is the most important process acting to remove contaminants from ground water, . The information also is useful when selecting the remedial alternative that will be most cost-effective in eliminating or abating these threats should natural attenuation not prove to be sufficient.

Over the past two decades, numerous laboratory and field studies have demonstrated that subsurface microorganisms can degrade a variety of hydrocarbons and chlorinated solvents (3, 23). Whereas fuel hydrocarbons are biodegraded through use as a primary substrate (electron donor), chlorinated aliphatic hydrocarbons may undergo biodegradation through three different pathways: through use as an electron acceptor, through use as an electron donor, or through co-metabolism, where degradation of the chlorinated organic is fortuitous and there is no benefit to the microorganism. Although at many sites the use of chlorinated aliphatic hydrocarbons as electron acceptors appears to be most important, under natural conditions at a given site, one or all of these processes may be operating (Figure 1). For example, Figure 1 shows vinyl chloride can aerobically mineralize to CO₂, aerobically cometabolize to CO₂ in the presence of toluene, aerobically cometabolize to CO₂ in the presence of methane, and reductively dechlorinate to ethene. In general, but in the electron acceptor pathway especially, biodegradation of chlorinated solvents will be an electron-donor-limited process. Conversely, biodegradation of fuel hydrocarbons is an electron-acceptor-limited process.

In a pristine aquifer, native organic carbon is used as an electron donor, and dissolved oxygen (DO) is used first as the prime electron acceptor. Where anthropogenic carbon (e.g., fuel hydrocarbon) is present, it also will be used as an electron donor. Following DO consumption, anaerobic microorganisms typically use additional electron acceptors (as available) in the following order of preference: nitrate, ferric iron oxyhydroxide, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron accepting compounds can provide evidence of where and how chlorinated aliphatic hydrocarbon biodegradation is occurring. In addition, because chlorinated aliphatic hydrocarbons may be used as electron acceptors or electron donors (in competition with other acceptors or donors), isopleth maps showing the distribution of the electron acceptor/donor compounds can provide evidence of the mechanisms of biodegradation working. As with BTEX, the driving force behind oxidation-reduction reactions resulting in chlorinated aliphatic hydrocarbon degradation is electron transfer. Although thermodynamically favorable, most of the reactions involved in chlorinated aliphatic hydrocarbon reduction and oxidation do not proceed abiotically. Microorganisms are capable of carrying out the reactions, but they will facilitate only those oxidation reduction reactions that have a net yield of energy.

⁵ Among the available models are MT3D, BIOMOD3D, BioREDOX, RT3D and others.

Mechanisms of Chlorinated Aliphatic Hydrocarbon Biodegradation

Electron Acceptor Reactions (Reductive Dechlorination)

The most important process for the natural biodegradation of the more highly chlorinated solvents is reductive dechlorination. During the reductive dechlorination, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. In general, reductive dechlorination occurs by sequential dechlorination, for example, reductive dechlorination from perchloroethene to trichloroethene to dichloroethene to vinyl chloride to ethene. Depending on environmental conditions, the reductive dechlorination process sequence may be interrupted, with other processes then acting on the products. Reductive dechlorination of chlorinated solvent compounds is associated with all accumulation of daughter products and an increase in the concentration of chloride ions.

Reductive dechlorination affects each of the chlorinated ethenes differently. Of the chlorinated ethene compounds, perchloroethene is the most susceptible to reductive dechlorination because it is the most oxidized. Conversely, vinyl chloride is the least susceptible to reductive dechlorination because it is the least oxidized of these compounds. The rate of reductive dechlorination also has been observed to decrease as the degree of chlorination decreases (24, 25). Murray and Richardson (26) have postulated that this rate decrease may explain the accumulation of vinyl chloride in perchloroethene and trichloroethene plumes that are undergoing reductive dechlorination.

Reductive dechlorination has been demonstrated under nitrate-reducing and sulfate-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under methanogenic conditions (24). Nitrate/sulfate-reducing condition discussion will be presented in greater detail in subsequent parts of this document. Because chlorinated aliphatic hydrocarbon compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth to occur (24). Potential carbon sources include natural organic matter, fuel hydrocarbons, or other organic compounds such as those found in landfill leachate.

Electron Donor Reactions

Murray and Richardson (26) write that microorganisms are generally believed to be incapable of growth using trichloroethene and perchloroethene as a primary substrate (i.e., electron donor). Under aerobic and some anaerobic conditions, the less-oxidized chlorinated aliphatic hydrocarbons (e.g., vinyl chloride) can be used as the primary substrate in biologically mediated redox reactions (22). In the electron donor reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. Fuel hydrocarbons are biodegraded by the electron donor process.

In contrast to reactions in which the chlorinated aliphatic hydrocarbon is used as an electron acceptor, only the least oxidized chlorinated aliphatic hydrocarbons can be used as electron donors in biologically mediated redox reactions. McCarty and Semprini (22) describe investigations in which vinyl chloride and 1,2-dichloroethane were shown to serve as primary substrates under aerobic conditions. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. In addition, Bradley and Chapelle (27) show evidence of mineralization of vinyl chloride under iron reducing conditions so long as there is sufficient bioavailable iron(III). Aerobic metabolism of vinyl chloride may be characterized by a loss of vinyl chloride mass and a decreasing molar ratio of vinyl chloride to other chlorinated aliphatic hydrocarbon compounds.

Co-metabolism

When a chlorinated aliphatic hydrocarbon is biodegraded via co-metabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated aliphatic hydrocarbon; in fact, the co-metabolic degradation of the chlorinated aliphatic hydrocarbon may be harmful to the microorganism responsible for the production of the enzyme or cofactor (22).

Co-metabolism is best documented in aerobic environments, although it could occur under anaerobic conditions. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of perchloroethene, are susceptible to co-metabolic degradation (22, 23, 26). Vogel (23) further elaborates that the co-

metabolism rate increases as the degree of dechlorination decreases. During co-metabolism, trichloroethene is indirectly transformed by bacteria as they use BTEX or another substrate to meet their energy requirements. Therefore, trichloroethene does not enhance the degradation of BTEX or other carbon sources, nor will its co-metabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources.

Behavior of Chlorinated Solvent Plumes

Chlorinated solvent plumes can exhibit three types of behavior depending on the amount of solvent, the amount of biologically available organic carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors being used. It must be noted that individual plumes may exhibit all three types of behavior in different portions of the plume. The different types of plume behavior are summarized below.

Type 1 Behavior

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and this anthropogenic carbon drives reductive dechlorination. When evaluating natural attenuation of a plume exhibiting Type 1, behavior the following questions must be answered:

1. Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms "strangle" before they "starve", will they run out of chlorinated aliphatic hydrocarbons (electron acceptors) before they run out of electron donors?
2. What is the role of competing electron acceptors (e.g., DO, nitrate, iron(III), and sulfate)?
3. Is vinyl chloride oxidized, or is it reduced?

Type 1 behavior results in the rapid and extensive degradation of the highly chlorinated solvents such as perchloroethene, trichloroethene, and dichloroethene.

Type 2 Behavior

Type 2 behavior dominates in areas that are characterized by relatively high concentrations of biologically available native organic carbon. This natural carbon source drives reductive dechlorination (i.e., is the primary substrate for microorganism growth). When evaluating natural attenuation of a Type 2 chlorinated solvent plume, the same questions as those posed for Type 1 behavior must be answered. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon contents) this type of behavior also can result in rapid degradation of chlorinated solvent compounds.

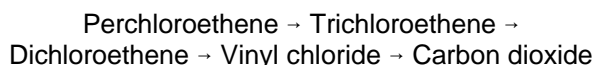
Type 3 Behavior

Type 3 behavior dominates in areas that are characterized by low concentrations of native and/or anthropogenic carbon and by DO concentrations greater than 1.0 milligrams per liter. Under these aerobic conditions, reductive dechlorination will not occur; thus, there is no removal of perchloroethene, trichloroethene, and dichloroethene. Advection, dispersion, and sorption are the most significant natural attenuation mechanisms for perchloroethene, trichloroethene, and dichloroethene in this setting. However, vinyl chloride can be rapidly oxidized under these conditions.

Mixed Behavior

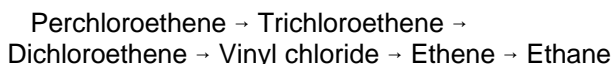
A single chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated aliphatic hydrocarbon plumes. For example, Wiedemeier et al. (28) describe a plume at Plattsburgh Air Force Base, New York, that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. The most fortuitous scenario involves a plume in which perchloroethene, trichloroethene, and dichloroethene are reductively dechlorinated

(Type 1 or 2 behavior), then vinyl chloride is oxidized (Type 3 behavior) either aerobically or via iron reduction. Vinyl chloride is oxidized to carbon dioxide in this type of plume and does not accumulate. The following sequence of reactions occurs in a plume that exhibits this type of mixed behavior:



The trichloroethene, dichloroethene, and vinyl chloride may attenuate at approximately the same rate, and thus these reactions may be confused with simple dilution. Note that no ethene is produced during this reaction. Vinyl chloride is removed from the system much faster under these conditions than it is under vinyl chloride-reducing conditions.

A less desirable scenario, but one in which all contaminants may be entirely biodegraded, involves a plume in which all chlorinated aliphatic hydrocarbons are reductively dechlorinated via Type 1 or Type 2 behavior. Vinyl chloride is chemically reduced to ethene, which may be further reduced to ethane or methane. The following sequence of reactions occurs in this type of plume:



This sequence has been investigated by Freedman and Gosseft (13). In this type of plume, vinyl chloride degrades more slowly than trichloroethene and thus vinyl chloride tends to accumulate.

Protocol for Quantifying Natural Attenuation During the Remedial Investigation Process

The primary objective of the natural attenuation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations in ground water to below risk-based corrective action or regulatory levels within an acceptable distance and/or time frame. The natural attenuation investigation requires a prediction of the potential extent and concentration of the contaminant plume in time and space. The prediction should be based on historic variations in, and the current extent and concentrations of, the contaminant plume, as well as the measured rates of contaminant attenuation. Because of the inherent uncertainty associated with such predictions, the investigator must provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. The demonstration requires the use of conservative solute fate-and-transport model input parameters and numerous sensitivity analyses so that consideration is given to all plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently supports the natural reduction and removal of the dissolved contaminant plume.

Figure 2 outlines the steps involved in the natural attenuation demonstration. Figure 2 also shows the important regulatory decision points in the process of implementing natural attenuation. Predicting the fate of a contaminant plume requires the quantification of solute transport and transformation processes.

Quantification of contaminant migration and attenuation rates and successful implementation of the natural attenuation remedial option requires completion of the following steps:

1. Review available site data, and develop a preliminary conceptual model.
2. Screen the site, and assess the potential for natural attenuation.
3. Collect additional site characterization data to support natural attenuation, as required.
4. Refine the conceptual model, complete premodeling calculations, and document indicators of natural attenuation.
5. Simulate natural attenuation using analytical or numerical solute fate-and-transport models that allow incorporation of a biodegradation term, as necessary.
6. Identify current and future receptors, and conduct an exposure-pathway analysis.
7. Determine whether source treatment will be remediation, removal, containment or a combination of these.

8. If natural attenuation (after source treatment) is acceptable, prepare a long-term monitoring plan.
9. Present findings to regulatory agencies.

Review Available Site Data, and Develop a Preliminary Groundwater Flow and Transport Conceptual Model

Existing site characterization data should be reviewed and used to develop a site-specific conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will allow placement of additional data collection points in the most scientifically advantageous and cost-effective manner. A site-specific conceptual model is a three-dimensional representation of the ground-water flow and solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data. This type of conceptual model differs from the conceptual site models that risk assessors commonly use that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. The groundwater system conceptual model, however, facilitates identification of these risk-assessment elements for the exposure pathways analysis. After development, the conceptual model can be used to help determine optimal placement of additional data collection points (as necessary) to aid in the natural attenuation investigation and to develop the solute fate-and-transport model.

Contracting and management controls must be flexible enough to allow for the potential for revisions to the conceptual model and thus the data collection effort. In cases where little or questionable site-specific data are available, all future site characterization activities should be designed to collect the data necessary to screen the site to determine the potential for remediation by natural attenuation. The data collected in support of natural attenuation can be used to design and support other remedial measures.

Table 1A. lists a standard set of methods, while Table 1B. lists methods that are under development and/or consideration for the soil and ground water analytical protocol for natural attenuation of chlorinated aliphatic hydrocarbons and/or fuel hydrocarbons. Any plan to collect additional ground-water and soil quality data should include targeting the analytes listed in Table 1A., and Table 1B., where the technique is finalized.

Screen the Site, and Assess the Potential for Natural Attenuation

After reviewing available site data and developing a preliminary groundwater flow and transport conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful in determining whether natural attenuation will be sufficient to prevent a dissolved contaminant plume from completing exposure pathways, or from reaching a predetermined point of compliance, in concentrations above applicable regulatory or risk-based corrective action standards. Determining the likelihood of exposure pathway completion is an important component of the natural attenuation investigation. The determination is achieved by estimating the migration and future extent of the plume based on contaminant properties, including volatility, sorptive properties, and biodegradability; aquifer properties, including hydraulic gradient, hydraulic conductivity, effective porosity, and total organic carbon (TOC) content; and the location of the plume and contaminant source relative to potential receptors (i.e., the distance between the leading edge of the plume and the potential receptor exposure points). These parameters (estimated or actual) are used in the example that follows to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

If, after completing the steps outlined in this Quantification of biological natural attenuation section, it appears that natural attenuation will be a significant factor in contaminant removal, detailed site characterization activities in support of the natural attenuation remediation is necessary. If exposure pathways have already been completed and contaminant concentrations exceed regulatory levels, or if such completion is likely, other remedial measures should be considered, possibly in conjunction with natural attenuation. Even so, the collection of data in support of the natural attenuation option can be integrated into a comprehensive remedial

plan and may help reduce the cost and duration of other remedial measures, such as intensive source removal operations or pump-and-treat technologies. For example, dissolved iron concentrations can have a profound influence on the design of pump-and-treat systems.

The screening process presented in this Quantification of biological natural attenuation section is outlined in Figure 3. The screening process allows the investigator to determine whether natural attenuation is likely to be a viable remedial alternative before additional time and money are expended. The data required to make the preliminary assessment of natural attenuation can also be used to aid the design of an engineered remedial solution, should the screening process suggest that natural attenuation alone is not feasible. The following information is required for the screening process:

- The chemical and geochemical data presented in Table 2 for monitoring wells located in zones upgradient, within the plume and downgradient. Figures 4A and 4B show the approximate locations of data collection points all of which are substantiated in the appropriate flow and contaminant site investigation. If other contaminants are suspected, then data on the concentration and distribution of these compounds also must be obtained.
- Locations of source(s) and receptor(s).
- An estimate of the contaminant transport velocity and direction of ground-water flow.

Once these data have been collected, the screening process can be undertaken. The following steps summarize the screening process:

1. Determine whether biodegradation is occurring using geochemical data. If biodegradation is occurring, proceed to Step 2. If it is not, assess the amount and types of data available. If data are insufficient to determine whether biodegradation is occurring, collect supplemental data.
2. Determine ground-water flow and solute transport parameters. Hydraulic conductivity and effective porosity may be estimated, but the ground-water gradient and flow direction may not. The investigator should use the highest hydraulic conductivity measured at the site during the preliminary screening because solute plumes tend to follow the path of least resistance (i.e., highest hydraulic conductivity). This will give the "worst case" estimate of solute migration over a given period.
3. Locate sources and current and future receptor exposure points.
4. Estimate the biodegradation rate constant. In ideal cases, biodegradation rate constants can be estimated using a conservative tracer found co-mingled with the contaminant plume, as described by Wiedemeier et al. (36). When dealing with a plume that contains only chlorinated solvents, this procedure will have to be modified to use chloride as a tracer. Rate constants derived from microcosm studies can also be used. If it is not possible to estimate the biodegradation rate using these procedures, then use a range of accepted literature values for biodegradation of the contaminants of concern.
5. Compare the rate of transport to the rate of attenuation, using analytical solutions or a screening model such as BIOSCREEN.
6. Determine whether the screening criteria are met.

Each step is described in detail below.

Step 1: Determine Whether Biodegradation Is Occurring

The first step in the screening process is to sample a minimum of six nested well location areas that are representative of the contaminant flow system and to analyze the samples for the parameters listed in Table 2. Samples should be taken 1) from the most contaminated portion of the aquifer (within or as close to the source area as possible); 2) downgradient from the source area, in the dissolved contaminant plume (2 sample locations); 3) downgradient from the dissolved contaminant plume; and 4) from upgradient and lateral locations that are not affected by the plume.

Samples collected in the Source Area allow determination of the dominant terminal electron-accepting processes at the site. Figure 5 is supplied in order to illustrate the hierarchy of the terminal electron-accepting

process. In conjunction with samples collected in the Source Area, samples collected in the Dissolved Contaminant Plume downgradient from the Source Area allow the investigator to determine whether the plume is degrading with distance along the flow path and what the distribution of electron acceptors and donors and metabolic byproducts might be along the flow path. The sample collected downgradient from the Dissolved Contaminant Plume aids in plume delineation and allows the investigator to determine whether metabolic byproducts are present in an area of ground water that has apparently been unaffected by the source. The upgradient and lateral samples allow delineation of the plume and indicate background concentrations of the electron acceptors and donors.

After these samples have been analyzed for the parameters listed in Table 2 (groundwater matrix parameters), the investigator should analyze the data to determine whether biodegradation is occurring. The reason for using the water (groundwater) matrix only in the analysis described in the previous sentence is because the scoring procedure is based on ground water concentrations and parameter data. The right-hand column of Table 2 contains scoring values that can be used for this task. For example, if the DO concentration in the area of the plume with the highest contaminant concentration is less than 0.5 milligrams per liter, this parameter is awarded 3 points. Table 3 summarizes the range of possible scores and gives an interpretation for each score. If the site scores a total of 15 or more points, biodegradation is probably occurring, and the investigator can proceed to Step 2. This method relies on the fact that biodegradation will cause predictable changes in ground-water chemistry.

Table 3. Interpretation of Points Awarded During Screening Step I

<u>Score</u>	<u>Interpretation</u>
0 to 5	Inadequate evidence for biodegradation of chlorinated organics
6 to 14	Limited evidence for biodegradation of chlorinated organics
15 to 20	Adequate evidence for biodegradation of chlorinated organics
> 20	Strong evidence for biodegradation of chlorinated organics

Consider the following two examples. Example 1 contains data for a site with strong evidence that reductive dechlorination is occurring. Example 2 contains data for a site with strong evidence that reductive dechlorination is not occurring.

Example 1. Strong Evidence for Biodegradation of Chlorinated Organics

<u>Analyte</u>	<u>Concentration in Contaminated Zone</u>	<u>Most points Awarded</u>
DO	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron(II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	5 mg/L	3
Oxidation/ reduction potential	-190 mv	2

Example 1. Strong Evidence for Biodegradation of Chlorinated Organics (cont.)

<u>Analyte</u>	<u>Concentration in Contaminated Zone</u>	<u>Most points Awarded</u>
Chloride	3x background	2
Perchloroethene (released)	1,000 mg/L	0
Trichloroethene (none released)	1,200 ug/L	2
cis-1,2-DCE (none released)	500 ug/L	2
Vinyl chloride (none released)	50 ug/L	2
Total points awarded	23	

In this example, the investigator can infer that biodegradation is occurring and may proceed to Step 2.

Example 2. Biodegradation of Chlorinated Organics Unlikely

<u>Analyte</u>	<u>Concentration in Most Contaminated Zone</u>	<u>Points Awarded</u>
DO	3 mg/l	-3
Nitrate	0.3 mg/L	2
Iron(II)	Not detected	0
Sulfate	10 mg/L	2
Methane	ND	0
Oxidation-reduction potential	100 mv	0
Chloride	Background	0
Trichloroethene (released)	1,200 ug/L	0
cis-1,2-Dichloroethene	Not detected	0
Vinyl chloride	ND	0
Total points awarded	1	

In this example, the investigator can infer that biodegradation is probably not occurring or is occurring too

slowly to be a viable remedial option. In this case, the investigator cannot proceed to Step 2 and will likely have to implement an engineered remediation system.

This scoring system was developed by Dr. John Wilson at EPA's RSKERC and Todd Wiedemeier of Parsons Engineering and has been peer reviewed.

Step 2: Determine Groundwater Flow and Solute Transport Parameters

If the interpretation of the score indicates biodegradation is occurring, it is important to quantify groundwater flow and solute transport parameters. U.S. EPA strongly recommends obtaining site specific parameter data for supporting natural attenuation to the fullest extent possible. Parameter Quantification will make it possible to use a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. To use an analytical model, it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of the effective porosity and dispersivity. The coefficient of retardation also is helpful to know. Quantification of these parameters is discussed by Wiedemeier et al. (1); the textbook Contaminant Hydrogeology (Fetter, 1992), The Soil Chemistry of Hazardous Materials (Dragun, 1988), Basics of Pump-and-Treat Ground-Water Remediation Technology (Mercer et al, 1990), Principles of Groundwater Engineering (Walton, 1991), and Ground Water Issue Paper Basic Concepts of Organic Contaminant Sorption at Hazardous Waste Sites (Piwoni et al, 1990) also contain information on these variables.

To make modeling as accurate as possible, the investigator must have site-specific hydraulic gradient and hydraulic conductivity data. To determine the ground-water flow and solute transport direction, the site must have at least three accurately surveyed wells, for the most simplistic site hydrogeologic conditions. The effective porosity and dispersivity are generally estimated using accepted literature values for the types of sediments found at the site. If the investigator does not have total organic carbon data for soil, the coefficient of retardation can still be estimated using default literature values for total organic carbon, soil bulk density, and the aquifer effective porosity; however, assuming that the solute transport and ground-water velocities are the same is usually conservative.

Step 3: Locate Sources and Receptor Exposure Points

To determine the length of flow for the predictive modeling conducted in Step 5, it is important to know the distance between the source of contamination, the downgradient end of the dissolved plume, and any potential downgradient or cross-gradient receptors.

Step 4: Estimate the Biodegradation Rate Constant

Estimated biodegradation rates can be used only after biodegradation has been shown to be occurring (see Step 1). The biodegradation rate is one of the most important model input parameters. Biodegradation of chlorinated aliphatic hydrocarbons can commonly be represented as a first-order rate constant. Site-specific biodegradation rates are required due to the sensitivity of this parameter to modeling results and because of the dependence biological degradation has on the physical properties of the site. If gathering site specific degradation rates is absolutely not possible the a method for obtaining this value should be negotiated with the technical parties for U.S. EPA.

Step 5: Compare the Rate of Transport to the Rate of Attenuation

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation is best accomplished using an analytical model. Several analytical models are available, but the BIOSCREEN model is probably the simplest currently available model to use. BIOSCREEN was developed to simulate biological degradation of hydrocarbons and the suggestions below should be incorporated into running the model for use on chlorinated solvent plumes. The model is nonproprietary and is available from the Robert S. Kerr Laboratory's home page on the Internet (www.epa.gov/ada/kerriab.html). The

BIOSCREEN model is based on Domenico's solution to the advection dispersion equation (38), and allows use of either a first-order biodegradation rate or an instantaneous reaction between contaminants and electron acceptors to simulate the effects of biodegradation. To model transport of chlorinated aliphatic hydrocarbons using BIOSCREEN, only the first-order decay rate option should be used. The model BIOCHLOR is under development by the Technology Transfer Division of Air Force Center for Environmental Excellence (AFCEE). The BIOCHLOR model will be geared towards evaluating transport of chlorinated compounds under the influence of biodegradation. BIOPLUME III is currently being peer reviewed by U.S. EPA and will be a numerical model that will simulate biological decay of organic compounds. Other models exist and a literature search for these models is recommended.

The primary purpose of comparing the rate of transport with the rate of attenuation is to determine whether the residence time along the flow path is adequate to be protective of human health and the environment (i.e., to qualitatively estimate whether the contaminant is attenuating at a rate fast enough to allow degradation of the contaminant to acceptable concentrations before receptors, or potential receptors, are reached). It is important to perform a sensitivity analysis to help evaluate the confidence in the preliminary screening modeling effort. If modeling indicates that natural attenuation may attain remedial action objectives, then the screening criteria are met, and the investigator can proceed with the natural attenuation feasibility study.

Step 6: Determine Whether the Screening Criteria Are Met

Before proceeding with the full-scale natural attenuation feasibility study, the investigator should ensure that the answers to all of the following criteria are "yes":

- Has the plume moved a distance less than expected, based on the known (or estimated) time since the contaminant release and the contaminant velocity, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, as well as estimates of effective porosity and contaminant retardation? The time of release is often difficult to ascertain and it is recommended that conferring with the regulatory and facility parties involved with the site be performed in order to prevent costly time and effort with an unsuitable time.
- Is it likely that the contaminant mass is attenuating at rates sufficient to be protective of human health and the environment at a compliance point, or point of discharge to a sensitive environmental receptor?
- Is the plume going to attenuate to concentrations less than risk-based corrective action guidelines or regulatory criteria before reaching potential receptors, or a compliance point?

Collect Additional Site Characterization Data To Support Natural Attenuation, As Required

Detailed site characterization is necessary to document the potential for natural attenuation. Review of existing site characterization data is particularly useful before initiating site characterization activities. Such review should allow identification of data gaps and guide the most effective placement of additional data collection points. There are two goals during the site characterization phase of a natural attenuation investigation. The first is to collect the data needed to determine whether natural mechanisms of contaminant attenuation are occurring at rates sufficient to protect human health and the environment. The second is to provide sufficient site-specific data to allow prediction of the future extent and concentration of a contaminant plume through solute fate and transport modeling. Because the burden of proof for natural attenuation is on the proponent, detailed site characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of natural attenuation requires that the following site-specific parameters be determined:

- The extent and type of soil and ground-water contamination.
- The location and extent of contaminant source area(s) (i.e., areas containing mobile or residual

NAPL).

- The potential for a continuing source due to leaking tanks or pipelines.
- Aquifer geochemical parameters.
- Regional hydrogeology, including ground water that is a current or potential source of drinking water or discharges into an ecologically sensitive area and regional confining units.
- Local and site-specific hydrogeology, including local drinking water supplies; location of industrial, agricultural, and domestic water wells; patterns of ground water use (current and future); lithology; site stratigraphy, including identification of transmissive and nontransmissive units; grain-size distribution (sand versus silt versus clay); partitioning coefficients; aquifer hydraulic conductivity; groundwater hydraulic information; preferential flow paths; locations and types of surface water bodies; and areas of local ground-water recharge and discharge.
- Identification of potential exposure pathways and receptors.

The following sections describe the methodologies that should be implemented to allow successful site characterization in support of natural attenuation. Additional information can be obtained from Wiedemeier et al. (1, 37).

Soil Characterization

To adequately define the subsurface hydrogeologic system and to determine the amount and three-dimensional distribution of contaminant mass that can act as a continuing source of ground-water contamination, extensive soil characterization must be completed. Soil characterization may have been completed during previous remedial investigation activities. The results of soils characterization will be used as input into a solute fate-and-transport model to help define a contaminant source term and to support the natural attenuation investigation.

The analytical protocol to be used for soil, aquifer matrix and soil gas sample analysis is presented in Table 1A. and 1B. The analytical methods includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Knowledge of the location, distribution, concentration, and total mass of contaminants of regulatory concern in soils or present as residual and/or mobile NAPL is required to calculate the mass transfer rate from the contaminant source to the ground water. Knowledge of the TOC content of the aquifer matrix is important for sorption and solute-retardation calculations. TOC samples should be collected from a background location in the stratigraphic horizon(s) where most contaminant transport is expected to occur. Oxygen and carbon dioxide measurements of soil gas can be used to find areas in the unsaturated zone where biodegradation is occurring. Knowledge of the distribution of contaminants in soil gas can be used as a cost-effective way to estimate the extent of soil volatile organic compound contamination.

Groundwater Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of natural attenuation, ground-water samples must be collected and analyzed. Biodegradation of organic compounds, whether natural or anthropogenic, brings about measurable changes in the chemistry of ground water in the affected area. By measuring these changes, documentation and quantitative evaluation of natural attenuation's importance at a site are possible.

Groundwater sampling is conducted to determine the concentrations and distribution of contaminants, daughter products, and ground-water geochemical parameters. The analytical protocol for ground-water sample analysis is presented in Table 1A. and 1B. The analytical protocol includes all of the parameters necessary to document natural attenuation, including the effects of sorption and biodegradation. Data obtained from the analysis of

ground water for these analytes is used to scientifically document natural attenuation and can be used as input into a solute fate-and-transport model. The following paragraphs describe each ground-water analytical parameter and the use of each analyte in the natural attenuation demonstration.

Volatile organic compound analysis (by Method SW8260a) is used to determine the types, concentrations, and distributions of contaminants and daughter products in the aquifer. Figure 1 (44) is included in the text for illustrative purposes. DO is the electron acceptor most thermodynamically favored by microbes for the biodegradation of organic carbon, whether natural or anthropogenic. Reductive dechlorination will not occur, however, if DO concentrations are above approximately 0.5 milligrams per liter. During aerobic biodegradation of a substrate, DO concentrations decrease because of the microbial oxygen demand. After DO depletion, anaerobic microbes will use nitrate containing compounds as an electron acceptor, followed by iron(III) containing compounds, then sulfate containing compounds, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the oxidation-reduction potential of the ground water further toward conditions that favor reductive dechlorination. The oxidation-reduction potential range of sulfate reduction and methanogenesis is optimal, but reductive dechlorination may occur under nitrate- and iron(III)-reducing conditions as well. Because reductive dechlorination works best in the sulfate reduction and methanogenesis oxidation-reduction potential range, competitive exclusion between microbial sulfate reducers, methanogens, and reductive dechlorinators can occur.

After DO has been depleted in the area of the plume where chlorinated aliphatic compounds are being anaerobically remediated (treatment zone), nitrate-containing compounds may be used as an electron acceptor for anaerobic biodegradation via denitrification. In some cases iron(III)-containing compounds are used as an electron acceptors during anaerobic biodegradation of electron donors. During this process, iron(III) is reduced to the more soluble iron(II). Iron(II) concentrations can thus be used as an indicator of anaerobic degradation of fuel compounds. After DO, nitrate, and bioavailable iron(III) have been depleted in the area of the plume where chlorinated aliphatic compounds are being anaerobically remediated, sulfate-containing compounds may be used as an electron acceptor for anaerobic biodegradation. This process is termed sulfate reduction and results in the production of sulfide-containing compounds. During methanogenesis (an anaerobic biodegradation process), carbon dioxide (or acetate)-containing compounds are used as an electron acceptors, and methane is produced. Methanogenesis generally occurs after oxygen, nitrates, bioavailable iron(III)s, and sulfates have been depleted in the treatment zone. The presence of methane in ground water is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane in ground water above background concentrations in contact with fuels is indicative of microbial degradation of fuel hydrocarbons.

The total alkalinity of a ground-water system is indicative of a water's capacity to neutralize acid. Alkalinity results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Alkalinity is important in the maintenance of ground-water pH because it buffers the ground-water system against acids generated during both aerobic and anaerobic biodegradation.

In general, areas contaminated by fuel hydrocarbons exhibit a total alkalinity that is higher than that seen in background areas. This is expected because the microbially mediated reactions causing biodegradation of fuel hydrocarbons cause an increase in the total alkalinity in the system. Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction, and are less pronounced during methanogenesis (40). In addition, Willey et al. (41) show that short-chain aliphatic acid ions produced during biodegradation of fuel hydrocarbons can contribute to alkalinity in ground water.

The oxidation-reduction potential of ground water is a measure of electron activity and an indicator of the relative tendency of a solution to accept or transfer electrons. Redox reactions in ground water containing organic compounds (natural or anthropogenic) are usually biologically mediated; therefore, the oxidation-reduction potential of a ground-water system depends on and influences rates of biodegradation. Knowledge of the oxidation-reduction potential of ground water also is important because some biological processes operate only within a prescribed range of redox conditions. The oxidation-reduction potential of ground water generally

ranges from -400 to 800 millivolts (mV). Figure 6 shows the typical redox conditions for ground water when different electron acceptors are used.

Oxidation-reduction potential can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the oxidation-reduction potential of the ground water while in the field helps the field scientist to determine the approximate location of the contaminant plume. To perform this task, it is important to have at least one redox measurement (preferably more) from a well located upgradient from the plume. Oxidation-reduction potential measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected ground-water samples (which can affect oxidation-reduction potential measurements), it is important to minimize potential aeration.

Dissolved hydrogen (gas) concentrations can be used to determine the dominant terminal electron-accepting process in an aquifer. Table 4 and Figure 5 are presented to respectively present the range of hydrogen concentrations for a given terminal electron-accepting process and the hierarchical scheme for diagnosing the terminal electron-accepting process. Much research has been done on the topic of using hydrogen measurements to delineate terminal electron-accepting processes (42,44). Because the efficiency of reductive dechlorination differs for methanogenic, sulfate-reducing, iron(III)-reducing, or denitrifying conditions, it is helpful to have hydrogen concentrations to help delineate redox conditions when evaluating the potential for natural attenuation of chlorinated ethenes in ground-water systems. Collection and analysis of ground-water samples for dissolved hydrogen content is not yet commonplace or standardized.

Table 4. Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

<u>Terminal Electron-Accepting Process</u>	<u>Hydrogen Concentration (nanomoles per liter)</u>
Denitrification	< 0.1
Iron(III) reduction	0.2 to 0.8
Sulfate reduction	1 to 4
Methanogenesis	> 5

Because the pH, temperature, and conductivity of a ground-water sample can change significantly shortly following sample acquisition, these parameters must be measured in the field in unfiltered, unpreserved, "fresh" water collected by the same technique as the samples taken for DO and redox analyses. The measurements should be made in a clean glass container separate from those intended for laboratory analysis, and the measured values should be recorded in the ground-water sampling record.

The pH of ground water has an effect on the presence and activity of microbial populations in the ground water. This is especially true for methanogens. Microbes capable of degrading chlorinated aliphatic hydrocarbons and petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units. Ground-water temperature directly affects the solubility of oxygen and other geochemical species. The solubility of DO is temperature dependent, being more soluble in cold water than in warm water. Ground-water temperature also affects the metabolic activity of bacteria. Rates of hydrocarbon biodegradation roughly double for every 10°C increase in temperature ("Q₁₀" rule) over the temperature range between 5°C and 25°C. Ground-water temperatures less than about 5°C tend to inhibit biodegradation, and slow rates of biodegradation are generally observed in such waters.

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases. Conductivity measurements are used to ensure that ground water samples collected at a site are representative

of the water in the saturated zone containing the dissolved contamination. If the conductivities of samples taken from different sampling points are radically different, the waters may be from different hydrogeologic zones.

Elemental chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl^- to Cl^{+7} , the chloride form (Cl^-) is the only form of major significance in natural waters (45). Chloride forms ion pairs or complexations with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (45). Chloride ions generally do not enter into oxidation-reduction reactions, form no important solute complexes with other ions unless the chloride concentration is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (45). Thus, physical processes control the migration of chloride ions in the subsurface, and chloride is an effective conservative tracer of ground-water contaminant plume migration.

During biodegradation of chlorinated hydrocarbons dissolved in ground water, chloride is released into the ground water. This process results in chloride concentrations in the ground water of the contaminant plume that are elevated relative to background concentrations. Because of the nonreactive behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates using methods similar to those discussed by Wiedemeier et al. (36).

Field Measurement of Aquifer Hydraulic Parameters

The properties of an aquifer that have the greatest impact on contaminant fate and transport include hydraulic conductivity, hydraulic gradient, effective porosity, and dispersivity. Estimating hydraulic conductivity and gradient in the field is fairly straightforward, but obtaining field-scale information on effective porosity and dispersivity can be difficult.

Therefore, most investigators rely on field data for hydraulic conductivity and hydraulic gradient and on literature values for effective porosity and dispersivity for the types of sediments present at the site. Methods for field measurement of aquifer hydraulic parameters are described by Wiedemeier et al. (1, 37). Additional sources of information is found in Groundwater (Freeze & Cherry, 1979), Applied Hydrogeology (Fetter, 1988), and Contaminant Hydrogeology (Fetter, 1993).

Microbiological Laboratory Data

Microcosm studies are used to show that the microorganisms necessary for biodegradation are present and to help quantify rates of biodegradation. If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of biodegradation. The most common technique used to show explicitly that microorganisms capable of degrading contaminants present at a site is the microcosm study. The results of a well-designed microcosm study will be easy for decision-makers with nontechnical backgrounds to interpret. Results of such studies are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Because microcosm studies are time-consuming and expensive, they should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of contaminants.

Biodegradation rate constants determined by microcosm studies often are much greater than rates achieved in the field. Microcosms are most appropriate as indicators of the potential for natural bioremediation and to prove that losses are biological, but it may be inappropriate to use them to generate rate constants. The preferable method of contaminant biodegradation rate-constant determination is in situ field measurement. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm, and the interpretation of the results of the microcosm study are presented by Wiedemeier et al. (1).

Refine the Conceptual Model, Complete Premodeling Calculations, and Document Indicators of Biological Degradation

Site investigation data should first be used to refine the conceptual model and quantify ground-water flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to help simulate natural attenuation over time. Because the burden of proof is on the proponent, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that natural attenuation is occurring.

Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered site characterization data to refine the preliminary conceptual model that was developed based on previously existing site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This conceptual model can then be used for contaminant fate-and-transport modeling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant contour (isopleth) maps, and electron acceptor and metabolic byproduct contour (isopleth) maps. Refinement of the conceptual model is described by Wiedemeier et al. (1).

Premodeling Calculations

Several calculations must be made prior to implementation of the solute fate-and-transport model. These calculations include sorption and retardation calculations, NAPL water-partitioning calculations, ground-water flow velocity calculations, and biodegradation rate-constant calculations. Each of these calculations is discussed in the following sections. Most of the specifics of each calculation are presented in the fuel hydrocarbon natural attenuation technical protocol by Wiedemeier et al. (1), and all will be presented in the protocol incorporating chlorinated aliphatic hydrocarbon attenuation (37).

Biodegradation Rate Constant Calculations

Biodegradation rate constants are necessary to simulate accurately the fate and transport of contaminants dissolved in ground water. In many cases, biodegradation of contaminants can be approximated using first-order kinetics. To calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution and volatilization. Two methods for determining first-order rate constants are described by Wiedemeier et al. (36). One method involves the use of a biologically recalcitrant compound found in the dissolved contaminant plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (47) involves interpretation of a steady-state contaminant plume and is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (48). The first-order biodegradation rate constants for chlorinated aliphatic hydrocarbons are also presented (J. Wilson et al., Dallas Symposium Notes).

Simulate Natural Attenuation Using Solute Fate-and-Transport Models

Simulating natural attenuation using a solute fate and transport model allows prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation modeling is a tool that allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical, and biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterization will improve the validity of the modeling results. In some cases, straightforward analytical models of contaminant attenuation are adequate to simulate natural attenuation.

Several well-documented and widely accepted solute fate-and-transport models are available for simulating the fate-and-transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation. The use of solute fate-and-transport modeling in the natural attenuation investigation is described by Wiedemeier et al. (1).

Identify Potential Receptors, and Conduct an Exposure-Pathway Analysis

After the rates of natural attenuation have been documented and predictions of the future extent and concentrations of the contaminant plume have been made using the appropriate solute fate-and-transport model, the case for natural attenuation should combine all available data and information to present the basis for using this as a remedial option. Supporting the natural attenuation option generally will involve performing a receptor exposure-pathway analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and ground-water use scenarios and the 9 criteria in the Feasibility Study. The results of solute fate-and-transport modeling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate-and-transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site can be estimated.

Evaluate Source Control

Source removal, treatment or containment will be necessary to reduce plume expansion. Several technologies suitable for source reduction or removal are listed in Figure 2. Other technologies may also be used as dictated by site conditions and local regulatory requirements. Source removal can be very effective at limiting plume migration and decreasing the remediation time frame, especially at sites where biodegradation is contributing to natural attenuation of a dissolved contaminant plume.

Present Findings and Obtain Consensus for Remediation by Natural Attenuation

A natural attenuation remedial alternative will be evaluated using the nine criteria used to evaluate other remedial alternatives. All available site-specific data and information developed during the site characterization, conceptual model development, premodeling calculations, biodegradation rate calculation, ground-water modeling, model documentation, and long-term monitoring plan preparation phases of the natural attenuation investigation should be presented in a consistent and complementary manner during the Feasibility Study (FS)/ Corrective Measures Study (CMS) process. Evidence that natural attenuation is occurring at rates sufficient to meet regulatory requirements, and to protect human health and the environment will be presented during the FS/CMS or Remedial Design/Remedial Action (RD/RA) or Corrective Remedial Action (CRA) stage of site work. A "weight-of-evidence" argument is necessary to support this remedial option. For this reason, all model assumptions should be conservative, and all available evidence in support of natural attenuation must be presented with regulatory requirements in mind.

Acknowledgements

The following individuals have participated in the various iterations of review of this document: Curt Black, Jim Barksdale, Paul Osborne, Rich Muza, John Wilson, and Bill O'Steen. The Superfund/RCRA Ground Water Forum Solvents Workgroup comments on the AFCEE Protocol for *Evaluation of Natural Attenuation of Chlorinated Solvents in Ground Water* have also been valuable in the production of this document.

References

1. Wiedemeier, TH., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. San Antonio, TX: U.S. Air Force Center for Environmental Excellence.
2. National Research Council. 1993. In-situ bioremediation: When does it work? Washington, DC: National Academy Press.
3. Bouwer, E.J., B.E. Rittman, and R.L. McCarty. 1981. Anaerobic degradation of halogenated 1- and 2-carbon organic compounds. Environ. Sci. Technol. 15 (5):596-599.
4. Wilson, J.T, and B.H. Wilson. 1985. Biotransformation of trichloroethylene in soil. Appl. Environ. Microbiol. 49(1):242-243.
5. Miller, R.E., and F.R. Guengedch. 1982. Oxidation of trichloroethylene by liver microsomal cytochrome P-450: Evidence for chlorine migration in a transition state not involving trichloroethylene oxide. Biochemistry 21:1090-1097.
6. Nelson, M.J.K., S.O. Montgomery, E.J. O'Neill, and P.H. Pritchard. 1986. Aerobic metabolism of trichloroethylene by a bacterial isolate. Appl. Environ. Microbiol. 52 (2):949-954.
7. Bouwer, E.J., and J.P. Wright. 1988. Transformations of trace halogenated aliphatics in anoxic biofilm columns. J. Contam. Hydrol. 2:155-169.
8. Lee, M.D. 1988. Bioremediation of aquifers contaminated with organic compounds. CRC Crit. Rev. Environ. Control 18:29-89.
9. Litde, C.D., A.V. Palumbo, S.E. Herbes, M.E. Lidstrom, R.L. Tyndall, and P.J. Gilmer. 1988. Trichloroethylene biodegradation by a methane-oxidizing bacterium. Appl. Environ. Microbiol. 54(4):951-956.
10. Mayer, K.R, D. Grbi-Gaii, L. Semprini, and P.L. McCarty. 1988. Degradation of trichloroethylene by methanotrophic bacteria in a laboratory column of saturated aquifer material. Water Sci. Tech. 20(11/12):175-178.
11. Arciero, D., T. Vannelli, M. Logan, and A.B. Hooper. 1989. Degradation of trichloroethylene by the ammonia-oxidizing bacterium *Nitrosomonas europaea*. Biochem. Biophys. Res. Commun. 159:640-643.
12. Cline, RV., and J.J. Delfino. 1989. Transformation kinetics of 1,1,1-trichloroethane to the stable product 1,1-Dichloroethene. In: Biohazards of drinking water treatment. Chelsea, MI: Lewis Publishers.
13. Freedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55:2144-2151.
14. Folsom, B.R., P.J. Chapman, and P.H. Pritchard. 1990. Phenol and trichloroethylene degradation by *Pseudomonas cepacia* G4: Kinetics and interactions between substrates. Appl. Environ. Microbiol. 56(5):1279-1285.
15. Harker, A.R., and Y. Kim. 1990. Trichloroethylene degradation by two independent aromatic-degrading pathways in *Alcaligenes eutrophus* JMP134. Appl. Environ. Microbiol. 56(4):1179-1181.
16. Alvarez-Cohen, L.M., and P.L. McCarty. 1991. Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture. Appl. Environ. Microbiol. 57(1):228-

17. Alvarez-Cohen, L.M., and P.L. McCarty. 1991. Product toxicity and cometabolic competitive inhibition modeling of chloroform and trichloroethylene transformation by methanotrophic resting cells. Appl. Environ. Microbiol. 57(4):1031-1037.
18. DeStefano, T.D, J.M. Gossen, and SH. Zinder. 1991. Reductive dehalogenation of high concentrations of tetrachloroethene to ethene by an anaerobic enrichment culture in the absence of methanogenesis. Appl. Environ. Microbiol. 57(8):2287-2292.
19. Henry, S.M. 1991. Transformation of trichloroethylene by methanotrophs from a groundwater aquifer. Ph.D. thesis. Stanford University, Palo Alto, CA.
20. McCarty, P.L., P.V. Roberts, M. Reinhard, and G. Hopkins. 1992. Movement and transformations of halogenated aliphatic compounds in natural systems. In: Schnoor, J.L., ed. Fate of pesticides and chemicals in the environment. New York, NY: John Wiley & Sons.
21. Hartmans, S., and J.A.M. de Bont 1992. Aerobic vinyl chloride metabolism in *Mycobacterium aurum* Li. Appl. Environ. Microbiol. 58(4):1220-1226.
22. McCarty, P.L., and L. Semprini. 1994. Ground-water treatment for chlorinated solvents, In: Norris, R.D., R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward, eds. Handbook of bioremediation. Boca Raton, FL: Lewis Publishers.
23. Vogel, T.M. 1994. Natural bioremediation of chlorinated solvents. In: Norris, R.D., R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward, eds. Handbook of bioremediation. Boca Raton, FL: Lewis Publishers.
24. Bouwer, E.J. 1994. Bioremediation of chlorinated solvents using alternate electron acceptors. In: Norris, R.D., R.E. Hinchee, R. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bouwer, R.C. Borden, T.M. Vogel, J.M. Thomas, and C.H. Ward, eds. Handbook of bioremediation. Boca Raton, FL: Lewis Publishers.
25. Vogel, T.M., and P.L. McCarty. 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. Appl. Environ. Microbiol. 49(5):1080-1083.
26. Murray, W.D., and M. Richardson. 1993. Progress toward the biological treatment of C1 and C2 halogenated hydrocarbons. Crit. Rev. Environ. Sci. Technol. 23(3):195-217.
27. Bradley, P.M., and F.H. Chapelle. 1996. Anaerobic mineralization of vinyl chloride in Fe(III)-reducing aquifer sediments. Environ. Sci. Technol. 40:2084-2086.
28. Wiedemeier, T.H., L.A. Benson, J.T. Wilson, D.H. Kampbell, J.E. Hansen, and R. Miknis. 1996. Patterns of natural attenuation of chlorinated aliphatic hydrocarbons at Plattsburgh Air Force Base, New York. Platform abstracts presented at the Conference on Intrinsic Remediation of Chlorinated Solvents, Salt Lake City, UT, April 2.
29. U.S. EPA. 1986. Test methods for evaluating solid waste, physical and chemical methods, 3rd ed. SW-846. Washington, DC.
30. U.S. EPA. 1983. Methods for chemical analysis of water and wastes. EPA/16020-07-71. Cincinnati, OH.

31. Hach Co. 1990. Hach Company Catalog: Products for Analysis. Ames, IA.
32. American Public Health Association. 1992. Standard methods for the examination of water and wastewater, 18th ed. Washington, DC.
33. AFCEE. 1993. Handbook to support the Installation Restoration Program (IRP) remedial investigations and feasibility studies (RI/FS). U.S. Air Force Center for Environmental Excellence. September. Brooks Air Force Base, TX.
34. AFCEE. 1992. Environmental chemistry function Installation Restoration Program analytical protocols. June.
35. Kampbell, D.H., J.T. Wilson, and S.A. Vandegrift. 1989. Dissolved oxygen and methane in water by a GC headspace equilibrium technique. *Int. J. Environ. Anal. Chem.* 36:249-257.
36. Wiedemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1996. Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in groundwater. *Ground Water Monitoring and Remediation*. In press.
37. Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, J.T. Wilson, D.H. Kampbell, J.E. Hansen, P. Haas, and F.H. Chapelle. 1996. Technical protocol for natural attenuation of chlorinated solvents in groundwater. San Antonio, TX: U.S. Air Force Center for Environmental Excellence. In preparation.
38. Domenico, R.A. 1987. An analytical model for multidimensional transport of a decaying contaminant species. *J. Hydrol.* 91:49-58.
39. Domenico, P.A., and F.W. Schwartz. 1990. *Physical and chemical hydrogeology* New York, NY: John Wiley and Sons.
40. Morel, F.M.M., and J.G. Hering. 1993. *Principles and applications of aquatic chemistry*. New York, NY: John Wiley & Sons.
41. Willey, L.M., Y.K. Kharaka, T.S. Presser, J.B. Rapp, and I. Barnes. 1975. Short chain aliphatic acid anions in oil field waters and their contribution to the measured alkalinity. *Geochim. Cosmochim. Acta* 39:1707-1711.
42. Lovley, D.R., and S. Goodwin. 1988. Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reaction in aquatic sediments. *Geochim. Cosmochim. Acta* 52:2993-3003.
43. Lovley, D.R., F.H. Chapelle, and J.C. Woodward. 1994. Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Environ. Sci. Technol.* 28(7):1205-1210.
44. Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford, and D.A. Vroblesky. 1995. Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resour. Res.* 31:359-371.
45. Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper 2254.
46. Kaufman, W.J., and G.T. Orlob. 1956. Measuring ground water movement with radioactive and chemical tracers. *Am. Water Works Assn. J.* 48:559-572.
47. Buscheck, T.E.G., and C.M. Alcantar. 1995. Regression techniques and analytical solutions to

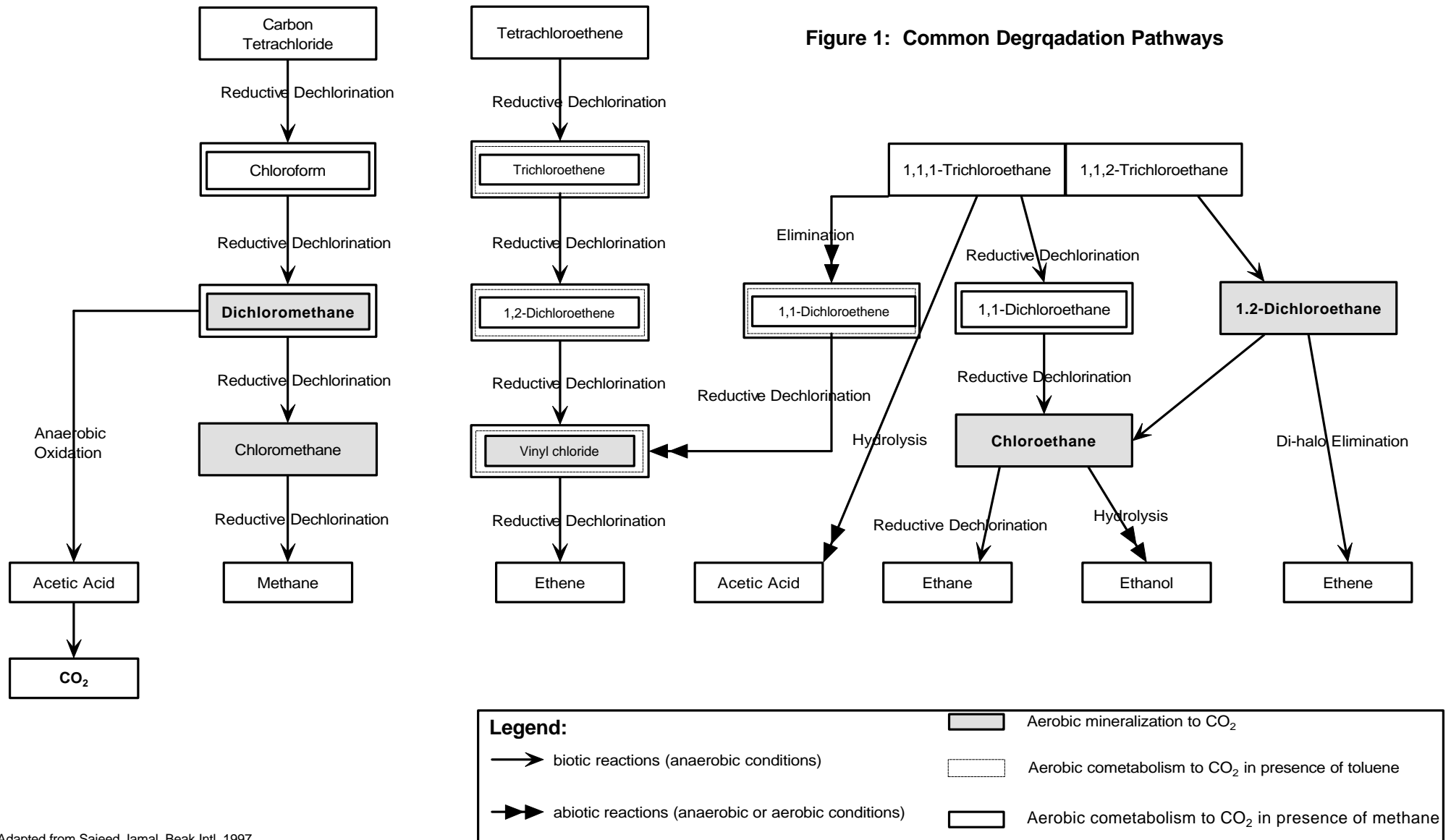
demonstrate intrinsic bioremediation. In: Proceedings of the 1995 Battelle International Conference on In-Situ and On Site Bioreclamation. April.

48. Bear, J. 1979. Hydraulics of groundwater. New York, NY McGraw-Hill.
49. Rice, D.W., R.D. Grose, J.C. Michaelson, B.P. Doohar, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.G. Everett, and M.A. Marino. 1995. California leaking underground fuel tank (LUFT) historical case analyses. California State Water Resources Control Board.

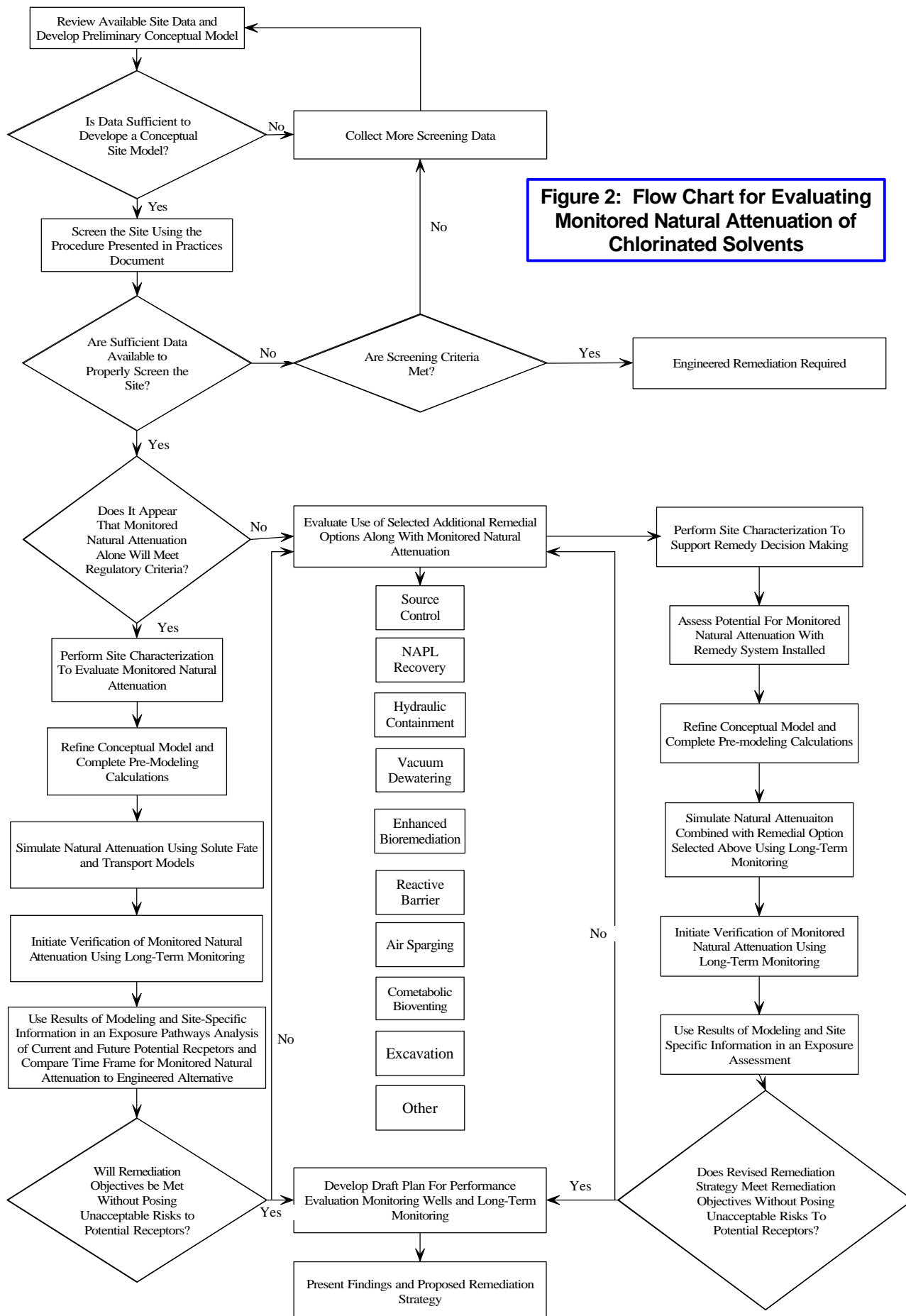
APPENDIX

Figures and Tables

Figure 1: Common Degrqadation Pathways



Adapted from Sajeed Jamal, Beak Intl, 1997



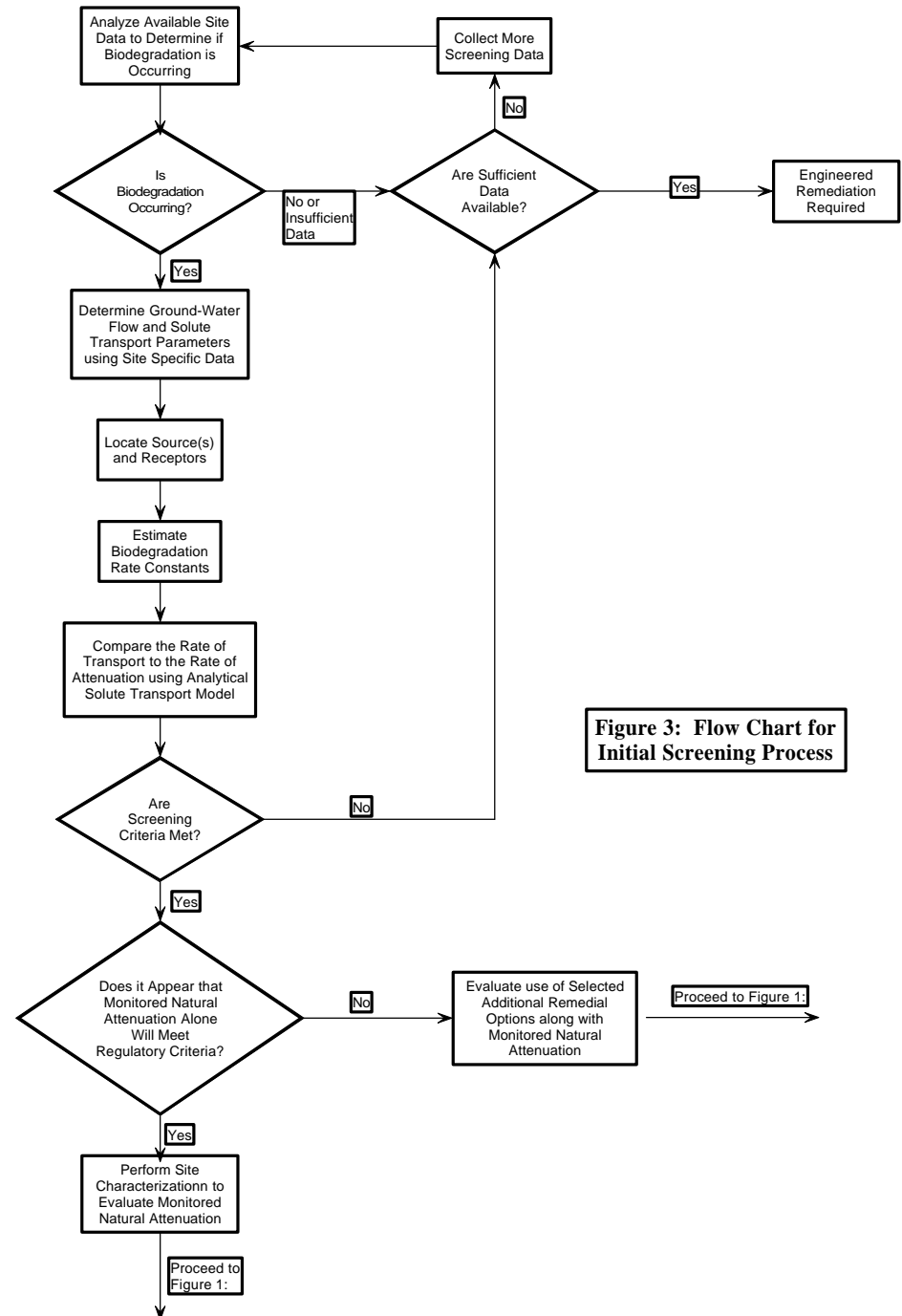


Figure 3: Flow Chart for Initial Screening Process

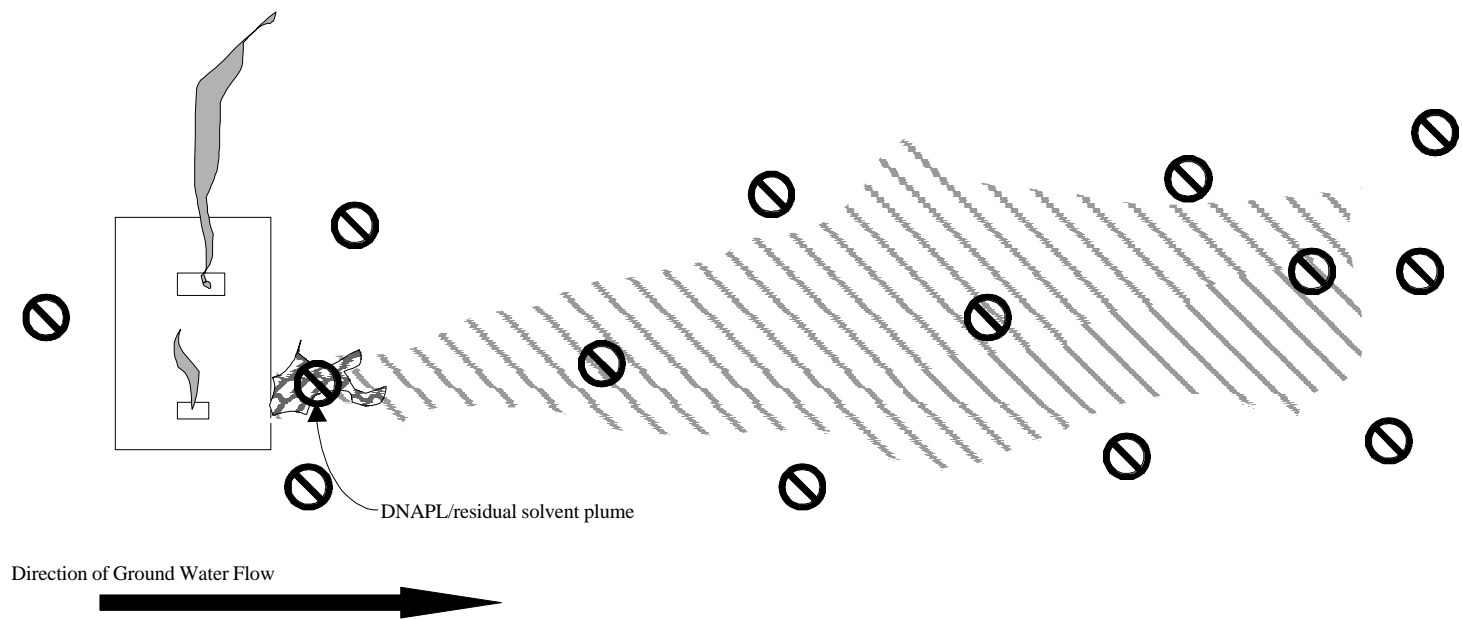
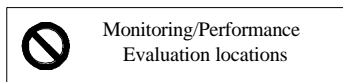
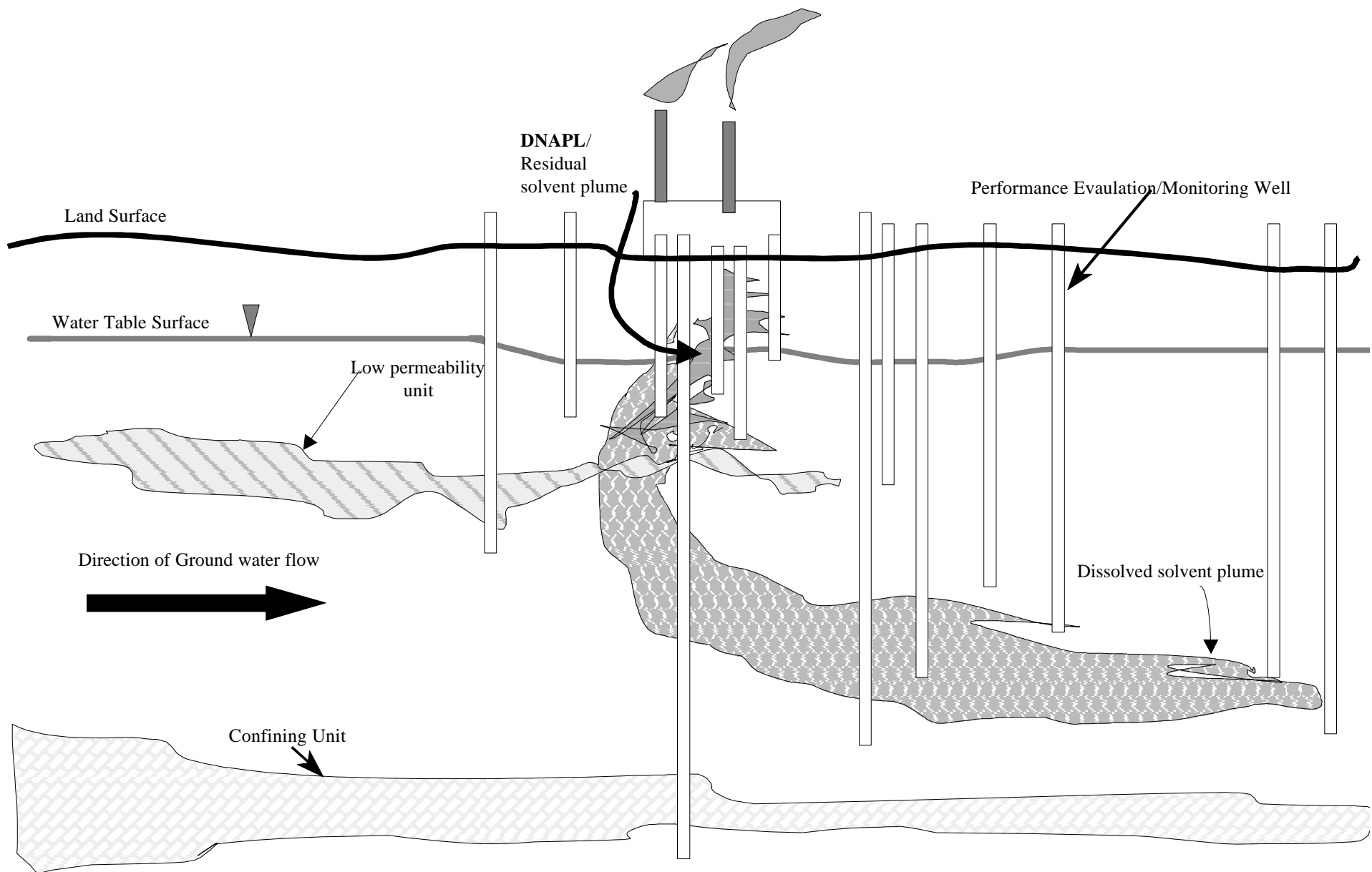


Figure 4A: Plan View of Generic Schematic for Monitoring/Performance evaluation well locations



Note: In some instances more wells will be required; In most instances nested wells will be necessary



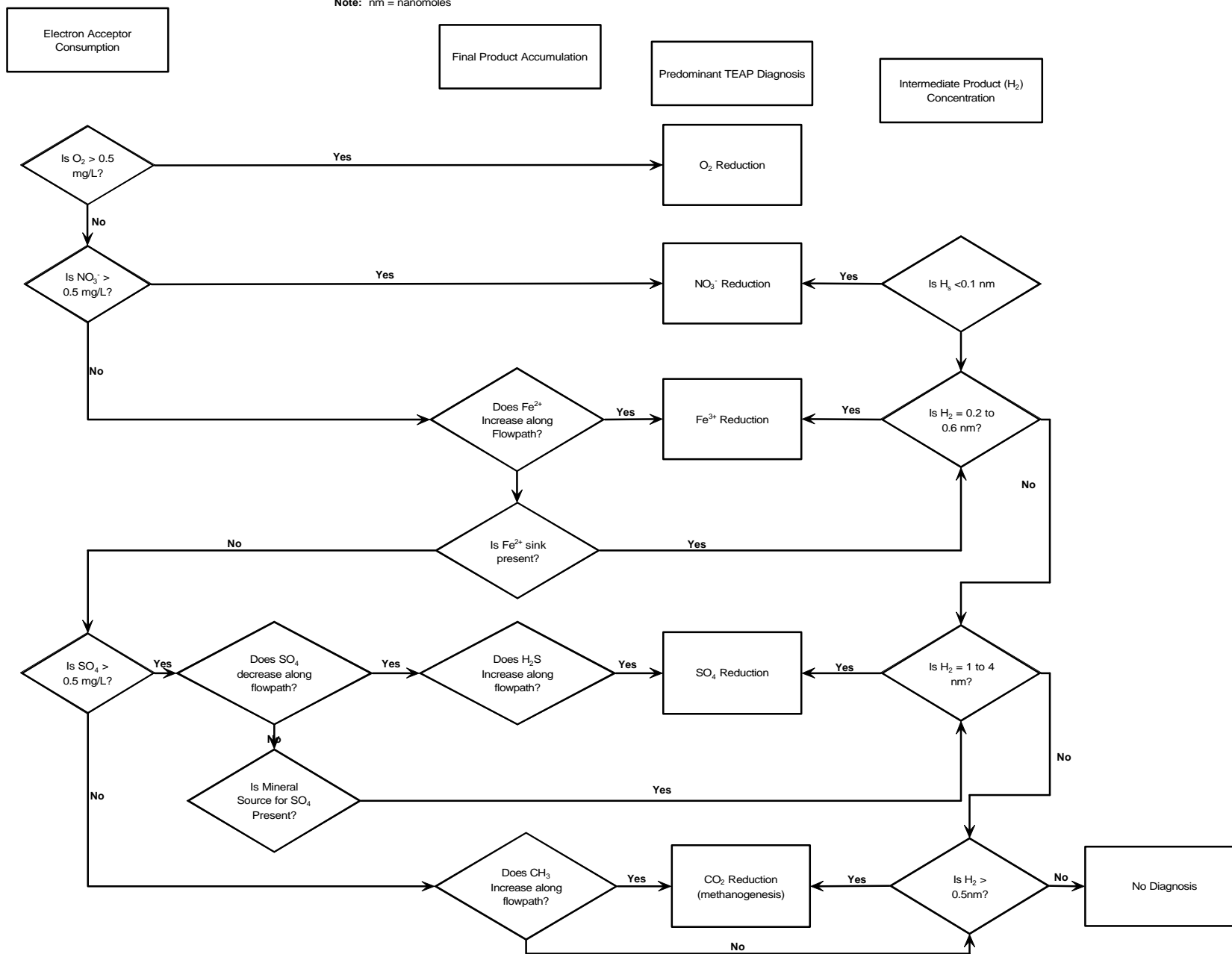
Note: In some areas of the plume more wells will be necessary; in most instances nested wells will be necessary

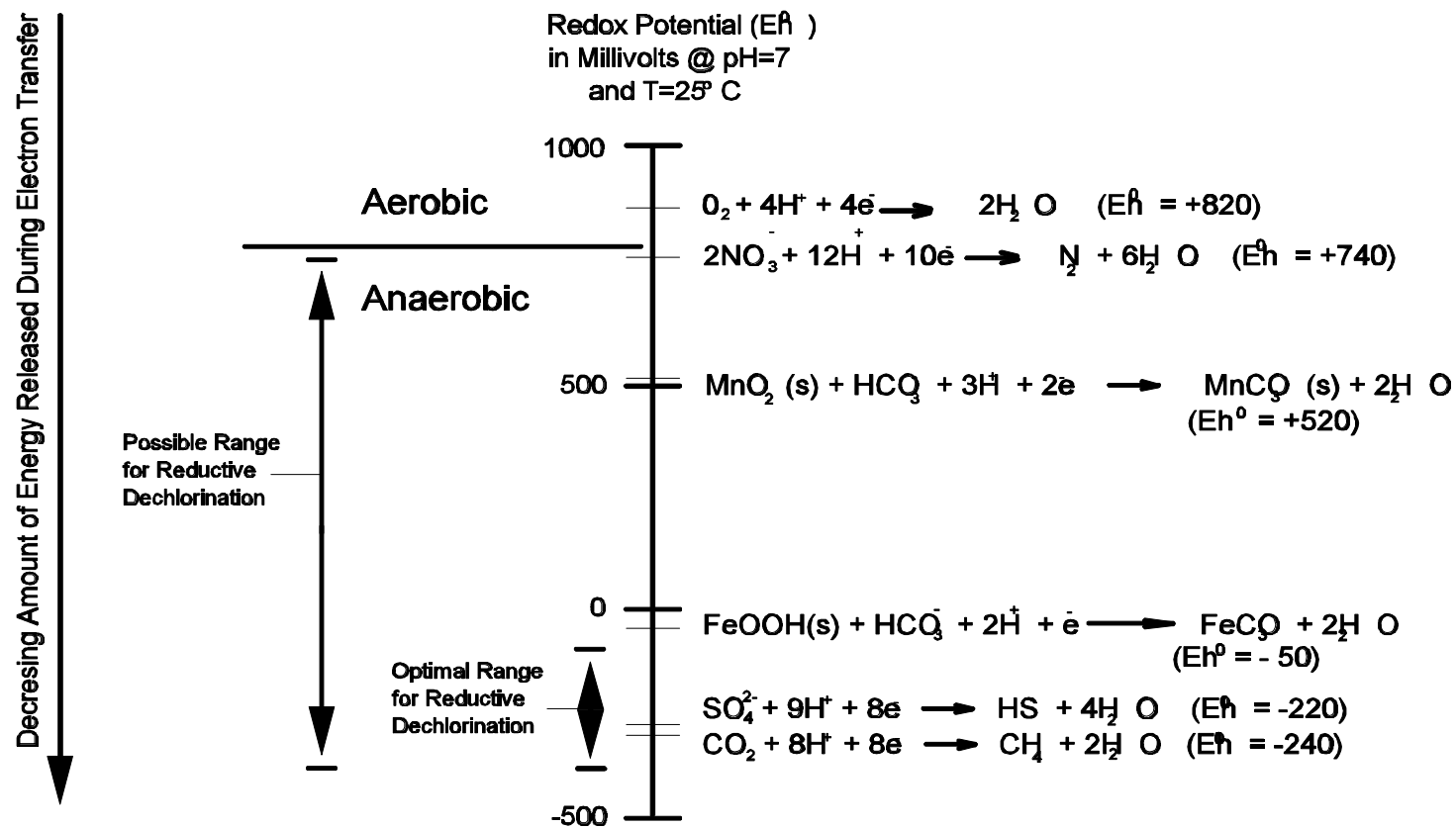
Figure 4B: A Generic Schematic of monitoring well/performance evaluation well placement

Figure 5: Hierarchical Scheme For Diagnosis of Terminal Electron-Accepting Processes¹ (TEAPs)

¹Taken from: "Deducing the Distribution of Terminal Electron-Accepting Processes in Hydrologically Diverse Groundwater Systems" Chapelle, et al., WRR, vol. 31, no. 2, pages 359-371, February 1995.

Note: nm = nanomoles





Modified From Bouwer (1994)

Figure 6. Redox potential for various electron acceptors.

Table 1A. Soil and Ground-Water Analytical Methods^a

All monitoring well installation, well development, well purging, sampling, sample handling and sample analysis where recommended will be performed in accordance with the May 1996 Region 4 ESD Environmental Investigations Standard Operating Procedures and Quality Assurance Manual (ESD EISOP-QAM available from <ftp://www.epa.gov/pub/r4ftp/sesd>).

Matrix	Analysis	Method/ Reference ^{b-e}	Comments ^{f,g}	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Contain, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Volatile Organic Compounds	SW8250A	Handbook method modified for field extraction of soil using methanol	Useful for determining the extent of soil contamination, the contaminant mass present and the need for source removal	Each soil sampling round	Sample volume approximately 100 mL; subsample and extract in the field using methanol or appropriate solvent; cool to 4° C	Fixed-base
Soil	Total Organic Carbon (TOC)	SW9060, modified for soil samples	Procedure must be accurate over the range of 0.1 to 5% TOC	The amount of TOC in the aquifer matrix influences contaminant migration and biodegradation	At initial sampling	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4° C	Fixed-base
Soil gas	Methane, O ₂ , CO ₂	Field soil gas analyzer		useful for determining the bioactivity in the vadose zone	At initial sampling and respiration testing	Reusable 3-L Tedlar bags	Field
Soil gas	Fuel and chlorinated volatile organic compounds	EPA Method TO -14		Useful for determining the distribution of chlorinated and BTEX compounds in soil	At initial sampling	1-L Summa canister	Fixed-base
Water	Aromatic and chlorinated hydrocarbons (BTEX), trimethylbenzene isomers, chlorinated compounds	SW8260A	Handbook method; analysis may be extended to higher molecular-weight alkyl benzenes	Method of analysis for BTEX and chlorinated solvents/byproducts which are the primary target analytes for monitoring biological degradation; method can be extended to higher molecular weight alkylbenzenes; trimethylbenzenes are used to monitor plume dilution if degradation is primarily anaerobic.	Each sampling round	Collect water samples in a 40-mL volatile organic analysis vial; cool to 4° C; add hydrochloric acid to pH2	Fixed-base
Water	Polycyclic aromatic hydrocarbons (PAHs) (intended for diesel and/or other heavy oils)	Gas chromatography Method SW8270B; high performance liquid chromatography Method SW8310	Analysis needed only when required for regulatory compliance	PAHs are components of fuel and are typically analyzed for regulatory compliance	As required by regulations	Collect 1 L of water in a glass container; cool to 4° C	Fixed-base

Table 1A.: Soil and Ground-Water Analytical Methods^a (continued)

Matrix	Analysis	Method/ Reference ^{b-e}	Comments ^{f,g}	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Contain, Sample Preservation	Field or Fixed-Base Laboratory
Water	Oxygen	DO meter (Note: DO meter should be calibrated between each well using the two point method); In the case of a sulfide ground water, the sulfide content of the ground water could cause false positives due to "poisoning" of the DO probe on the flow- through cell; in this instance use the Winkler kit and titrate.	Refer to Method A4500 for a comparable laboratory procedure.	Concentrations less than 1 mg/l generally indicate anaerobic pathway	Each sampling round	Measure DO on site using a flowthrough cell. A DO meter calibration is necessary and the flowthrough cell should be observed to make sure degassing is occurring, if so apparatus adjustment will be necessary.	Field
Water	Nitrate	IC method E- 300	Method E300 is a Handbook Method	Substrate for microbial respiration if oxygen is depleted	Each sampling round	Collect 40 mL of water in a glass or plastic container; add H ₂ SO ₄ to pH < 2, keep cool	Field
Water	Iron(II) (Fe ⁺²)	Colorimetric HACH Method 8146	Filter if turbid	May indicate an anaerobic degradation process due to depletion of oxygen, nitrate, and manganese	Each sampling round	Collect 100 mL of water in a headspace free container to eliminate introduction of oxygen and analyze as soon as possible	Field
Water	Sulfate (SO ₄ ⁻²)	Ion Chromotography Method E300 or HACH Method 8051	Method E300 is a Handbook method; do not use the field method if this method is used.	Substrate for anaerobic microbial respiration	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4° C	Fixed-base
Water	Sulfate (SO ₄ ⁻²)	HACH Method 8051	HACH Method 8051 is a colorimetric method, use one or the other consistently	Substrate for anaerobic microbial respiration	Each sampling round	Collect up to 40 mL of water in a glass or plastic container; cool to 4° C	Field
Water	Sulfide	HACH 2100 Spectrophotom- eter and specified reagents	Use this method consistently throughout investigation	Microbially reduced form of sulfate. Indicates reduced conditions. Also to evaluate whether the DO readings are false positives that are the result of sulfide interferences on the DO probe	Each sampling round	See HACH kit specifications	Field

Table 1A.: Soil and Ground-Water Analytical Methods^a (continued)

Matrix	Analysis	Method/ Reference ^{b-e}	Comments ^{f,g}	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Contain, Sample Preservation	Field or Fixed-Base Laboratory
Water	Methane, ethane and ethene	Kampbell et al, 1989 (35) or SW3810, modified	Method published by EPA researchers. Limited to few commercial labs.	The presence of CH ₄ suggests biodegradation of organic carbon via methanogenesis; ethane and ethene are produced during reductive dechlorination and the data is used where chlorinated solvents are suspected of undergoing biological transformation.	Each sampling round	Collect water samples in 50 mL glass serum bottles with butyl gray/Teflon-lined caps; add H ² SO ₄ to pH < 2; cool to 4 ⁰ C	Fixed-base
Water	Oxidation- reduction potential	A2580B	Measurements made with electrodes; results are displayed on a meter; protect samples from exposure to oxygen; report results against a silver/silver chloride reference electrode	The oxidation-reduction potential of ground water influences and is influenced by the nature of the biologically mediated degradation of contaminants; The oxidation-reduction potential of ground water may range from more than 800 mV to < -400 mV	Each sampling round	Collect 100 to 250 mL of water in a glass container, fulling container from bottom; analyze immediately	Field
Water	Conductivity	E120.1/ SW9050 direct reading meter	Protocols/ Handbook Methods	Water Quality parameter used as a marker to verify that the samples are obtained from the same ground-water system	Each sampling round	Collect 100 to 250 mL of water in a glass or plastic container	Field
Water	Major Cations	SW6010	Protocols/ Handbook Methods	Can be used to evaluate other remedial actions	Each sampling round	Collect 100 to 250 mL of water in a glass or plastic container	Field
Water	Chloride	IC Method E300	Method SW9050 may also be used	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system. Final product of chlorinated solvent reduction.	Each sampling round	Collect 250 mL of water in a glass container	Fixed-base
Water	Chloride (optional, see data use)	Hach Chloride test kit Model 8-P	Silver Nitrate titration	As above, and to guide selectino of additional data points in real time while in the field	Each Sampling round	Collect 100 mL of water in a glass container	Field
Water	Total Organic carbon	SW9060	Laboratory	Used to classify plume and to determine if cometabolism is possible in the absence of anthropogenic carbon	Each sampling round	Collect 100 mL of water in a glass container, cool	Laboratory

^a Analyses other than those listed in this table may be required for evaluation of biological degradation processes.

^b "SW" refers to the *Test methods for Evaluating Solid Waste, Physical, and chemical Methods* (29)

^c "E" refers to *Methods for Chemical Analysis of Water and Wastes* (30).

^d "HACH" refers to the Hach Company catalog (31).

^e "A" refers to *Standard Methods for the Examination of Water and Wastewater* (32).

^f "Handbook" refers to the AFCEE *Handbook to Support the Installation Restoration Program Analytical Protocols* (34)

^g "Protocols" refers to the AFCEE

NOTE: All monitoring well installation, well development, well purging, sampling, sample handling and sample analysis where recommended will be performed in accordance with the May 1996 Region 4 ESD *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual* (ESD EISOP-QAM)

Table 1B: Soil and Ground-Water Analytical Protocol: Special Analyses Under Development and/or Consideration^{a,b}

Matrix	Analysis	Method/ Reference ^{b-e}	Comments ^{f,g}	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Contain, Sample Preservation	Field or Fixed-Base Laboratory
Soil	Biologically available iron(III)	Under development	HCl extraction followed by quantification of released iron(III)	Optional method that should be used when fule hydrocarbons or vinyl chloride are present in the groundwater to predict the possible extent of removal of fule hydrocarbons and vinyl chloride via iron reduction.	One sampling round or as determined by site conditions	Collect minimum 1-inch diameter core samples into a plastic liner; cap and prevent aeration	Laboratory
Water	Hydrogen (H ₂)	Equilibration with gas in the field; determined with a reducing gas detector	Specialized analysis	To determine terminal electron accepting process; predicts the possibility for reductive dechlorination	At least one sampling round or as determined by site conditions	Sampling at well head requires the production of 100 mL per minute of water for 30 minutes	Field
Water	Nutritional quality of native organic matter	Under development	Spectro-photometric method	To determine the extent of reductive dechlorination allowed by the supply of electron donor	One round of sampling	Collect 1000 mL in an amber glass	Laboratory
Water	Oxygenates (including methyl-tert-butyl ether, ethers, acetic acid, methanol, and acetone)	SW8260/8015 ^c	Laboratory	Contaminant or electron donors for dechlorination of solvents	At least one sampling round or as determined by regulators	Collect L of water in a glass container; preserve with HCl	Laboratory

^a analyses other than those listed in this table may be required for regulatory compliance

^b Site characterization should not be delayed if these methods are unavailable

^c "SW" refers to the *Test methods for Evaluating Solid Waste, Physical, and chemical Methods* (29)

NOTE: EPA Region 4 is currently working on preparing a Protocol for sampling and analysis of certain field parameters for which there are no Standardized SOP's

Table 2: Analytical Parameters and Weighting for Preliminary Screening

Analyte	Concentration in Most Contaminated zone	Interpretation	Points Awarded
Oxygen ^a	< 0.5 mg/L	Tolerated; suppresses reductive dechlorination at higher concentrations	3
Oxygen ^a	> 1 mg/L	Vinyl chloride may be oxidized aerobically, but reductive dechlorination will not occur	-3
Nitrate ^a	< 1 mg/L	At higher concentrations may compete with reductive pathway at higher concentrations	2
Iron (II) ^a	> 1 mg/L	Reductive pathway possible; vinyl chloride may be oxidized under Fe(III)-reducing conditions	3
Sulfate ^a	< 20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide ^a	> 1 mg/L	Reductive pathway possible	3
Methane ^a	<0.5 mg/L	vinyl chloride oxidizes	0
Methane ^a	> 0.5 mg/L	Ultimate reductive daughter product, vinyl chloride accumulates	3
Oxidation reduction potential ^a (ORP)	< 50 mV <-100 mV	Reductive pathway possible Reductive pathway likely	1 2
pH ^a	5 < pH < 9 5 > pH > 9	Optimal range for reductive pathway Outside optimal range for reductive pathway	0 -2
TOC (total organic carbon)	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature	> 20°C	At T > 20°C, biochemical process is accelerated	1
Carbon Dioxide ^a	> 2 times background	Ultimate oxidative daughter product	1
Alkalinity	> 2 times background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride ^a	> 2 times background	Daughter product of organic chlorine	2
Hydrogen	> 1 nM	Reductive pathway possible; vinyl chloride may accumulate	3
Hydrogen	< 1 nm	Vinyl chloride oxidized	0
Volatile fatty acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX ^a	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Perchloroethene		Material Released	0
Trichloroethene ^a		Material released Daughter product of perchloroethene	0 2 ^b
Dichloroethene ^a		Material released or daughter product of trichloroethene Daughter product of trichloroethene if amount of cis-1,2-dichloroethene is greater than 80% of total dichloroethene, it is likely a daughter product of trichloroethene; 1,1-DCE can be chemical reaction product of TCA	0 2 ^a
Vinyl chloride ^a		Material released Daughter product of dichloroethene	0 2 ^b
Ethene/Ethane	> 0.01 mg/L > 0.1 mg/L	Daughter product of vinyl chloride/ethene	2 3
Dichloroethane		Daughter product of trichloroethene	2
Chloroethane ^a		Daughter product of vinyl chloride under reducing conditions	2

Analyte	Concentration in Most Contaminated zone	Interpretation	Points Awarded
1,1,1-Trichloroethane ^a		Material Released	0
Chloroform		Material Released Daughter product of Carbon Tetrachloride	0 2
Carbon Tetrachloride		Material Released	0
Dichloromethane		Material Released Daughter product of chloroform	0 2

^a Required Analysis

^b Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).